



TITLE:

Properties Control of Main Group Element π -Electron Systems Based on Coordination Number Change/
Substituent Effect on the Intramolecular Reactions of the [(Allyloxy)silyl]lithiums/ Phosphonium Sila-Ylide: Reaction Pathway Different from Ammoniu ...

AUTHOR(S):

TAMAO, Kohei; TOSHIMITSU, Akio; KAWACHI, Atsushi; YAMAGUCHI, Shigehiro; XU, Caihong; MAEDA, Hirofumi

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Prof
TAMAO, Kohei
(D Eng)



Assoc Prof
TOSHIMITSU, Akio
(D Eng)



Instr
KAWACHI, Atsushi
(D Eng)



Instr
YAMAGUCHI,
Shigehiro
(D Eng)



Res
XU, Caihong
(D Sc)



PD (JSPS)
MAEDA, Hirofumi
(D Eng)

Students

ITAMI, Yujiro (D3)	SHIRASAKA, Toshiaki (D3)
SAEKI, Tomoyuki (D2)	MINAMIMOTO, Takashi (D1)
KANETA, Yasuhiro (M2)	MIKI, Takashi (M2)
FUJIMURA, Hirokazu (M1)	KATAOKA, Takeshi (M1)
FUKAZAWA, Aiko (U4)	UMEHARA, Teruhiko (U4)

Visitor

FORSSIER, Kareen Ecole Polytechnique, France, 3 July
2001–23 August 2001

Scope of Research

Our research is concerned with some new aspects in the elemento-organic chemistry, including (1) the design and synthesis of novel π -conjugated systems containing main group elements such as boron and silicon for electronic and photonic applications, (2) the synthesis, structural studies, and synthetic applications of organosilicon compounds, such as pentacoordinate silicon compounds and functionalized silyl anions, (3) the elucidation of the σ -conjugation in the polysilane framework using the configuration-constrained oligosilane model systems, (4) the old but new chemistry of the disilapropellane and related compounds, and (5) the development of new efficient reactions using main group element reagents and transition metal complex catalysts.

Research Activities (Year 2001)

Presentations

Main Group Organic Chemistry Directed towards Materials Science: Photophysical Properties Control by Coordination Number Change, Tamao K, Yamaguchi S, JOM Symposium on New Frontiers in Organometallic Chemistry, 27–28 August, Chicago, USA.

Chemistry of 1,6-Disila[4.4.4]propellane and Related Compounds, Toshimitsu A, Katkevics M, Sano A, Asahara M, Miki T, Fujimura H, Tsuji H, Yamaguchi S, Tamao K, 18th International Congress of Heterocyclic Chemistry, 31 July, Yokohama, Japan.

Preparation and Reactions of Sulfur-Substituted Silyllithiums, Kawachi A, Oishi Y, Kataoka T, Tamao K, International Symposium on Reactive Intermediates and Unusual Molecules, 8–13 September, Nara, Japan.

Grants

Tamao K, Elements Science towards Construction of

Organic and Inorganic Frameworks Focusing on Quality of Elements, Grant-in-Aid for Scientific Research on COE, April 2000–March 2005.

Toshimitsu A, Chemistry of Propeller-Shaped Cyclic Compounds Bearing Disilane as an Axis, Grant-in-Aid for Scientific Research on Priority Areas (A) "Exploitation of Multi-Element Cyclic Molecules", April 2000–March 2001.

Kawachi A, Intramolecular Reactions of Functionalized Silyllithiums with Olefins: Development and Application to Stereoselective Synthesis, Grant-in-Aid for Scientific Research No. 12750763, April 2000–March 2002.

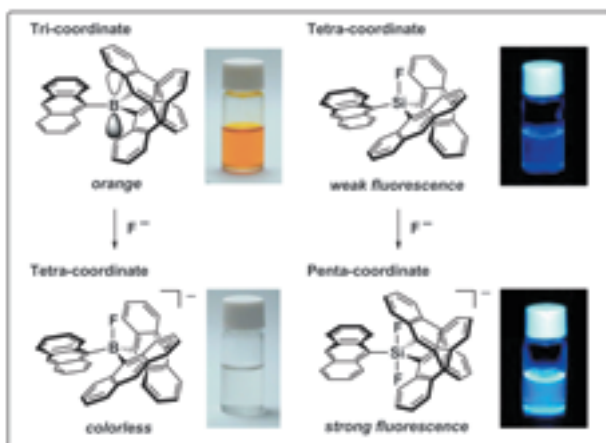
Kawachi A, New Reactions and Reactivity Control of Heteroatom-Substituted Silyl Anions, Grant-in-Aid for Scientific Research on "Molecular Physical Chemistry", No. 12042241, April 2000–March 2002.

Yamaguchi S, Elemento-Organic π -Electron Systems

Topics

Properties Control of Main Group Element π -Electron Systems Based on Coordination Number Change

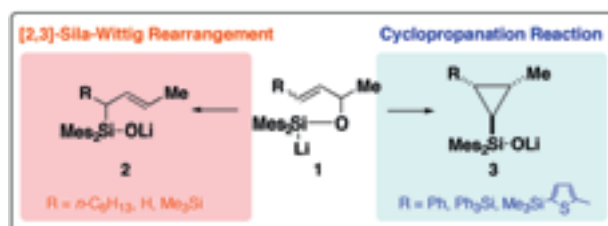
The incorporation of main group elements into π -conjugated framework enables access to new π -electron systems with intriguing photophysical and electronic properties and functions. We have explored a new possibility of controlling the properties of the π -electron systems based on a change in the coordination states of the elements. In a series of trianthryl derivatives of boron, silicon, and phosphorus, the control of the photophysical properties by changing the coordination number of the element has been achieved in various modes dependent on the element. In particular, the silicon and boron derivatives have new functions as the fluorescent and colorimetric fluoride sensors, respectively [1].



1. S. Yamaguchi, S. Akiyama, and K. Tamao, *J. Am. Chem. Soc.*, **123**, 11372 (2001).

Substituent Effect on the Intramolecular Reactions of the [(Allyloxy)silyl]lithiums

Whereas intramolecular reactions of organolithium reagents with olefins have been extensively studied in organic synthesis, less attention has been paid to the intramolecular reactions of silyllithium reagents with olefins despite the potential utility for the regio- and stereoselective Si-C bond formation. We have investigated the substituent effect on the intramolecular reaction of the [(allyloxy)silyl]lithiums and found that the reaction modes are strongly influenced by a substituent on the terminus of the olefins [2]. In the [(allyloxy)silyl]lithiums **1**, the trimethylsilyl group and non-substituent as well as the

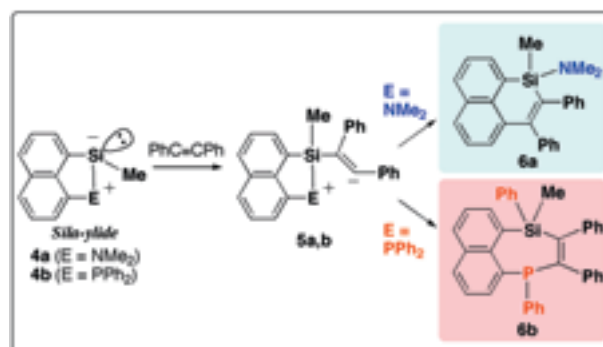


n-hexyl group cause the [2,3]-sila-Wittig rearrangement to afford **2** whereas the phenyl, triphenylsilyl, and thienyl groups cause the cyclopropanation reaction to yield **3**. Ab initio molecular orbital calculations revealed that the electronic effect of the substituents on the LUMO determines the reaction modes.

2. A. Kawachi, H. Maeda, H. Nakamura, N. Doi, and K. Tamao, *J. Am. Chem. Soc.*, **123**, 3143 (2001).

Phosphonium Sila-Ylide: Reaction Pathway Different from Ammonium Sila-Ylide

While a divalent silicon species, silylene, generally has an electrophilic character, we have recently clarified that intramolecularly amine-coordinated silylene **4a** behave as a nucleophilic sila-ylide. Thus, **4a** reacts with a trapping agent such as diphenylacetylene to afford a silaphenalene derivative **6a** via a zwitterionic intermediate **5**. In contrast to this, we have now disclosed that its phosphonium analog **4b** undergoes a reaction course completely different from that of **4a** [3]. Thus, **4b** affords a seven-membered cyclic product **6b**, through the incorporation of the acetylene between the silicon atom and the phosphorus atom accompanied by the migration of one phenyl group from phosphorus to silicon. This reaction seems to proceed through a pentavalent phosphorane intermediate or transition state structure.



3. A. Toshimitsu, T. Saeki, and K. Tamao, *J. Am. Chem. Soc.*, **123**, 9210 (2001).

for the Materials Science, PRESTO, Japan Science and Technology Corporation, December 2001–November 2004.

Award

Kawachi A, The Chemical Society of Japan Award for Distinguished Young Chemists, 29 March.